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PATH DEPENDENCE OF STRUCTURAL RELAXATION OF ELASTOMERIC
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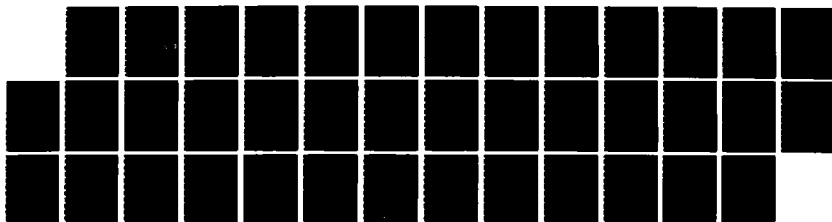
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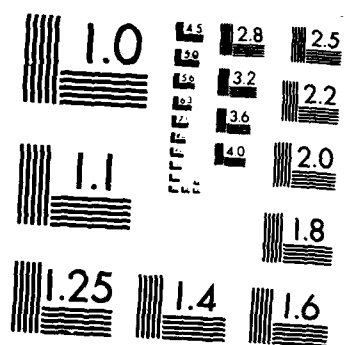
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$$\delta(t) = \delta_0 \phi(t, t_0) - \int_{t_0}^t (\Delta \alpha q - \Delta \beta p) \phi(t, t') dt'$$

where the relaxation time involved in ϕ is an explicit function of P , T , P_f (fictive pressure), and T_f (fictive temperature). T and T_f , and P and P_f are mutually convertible by a relationship, $d\delta = \Delta \beta d(P - P_f) = \Delta \alpha d(T_f - T)$ in which both $\Delta \beta$ and $\Delta \alpha$ are functions of P and T . During the aging of the elastomeric glass, Young's modulus (E) was measured at various intervals of aging time to monitor the variation of δ , the volumetric measure of departure from the equilibrium, related to E by an equation, $\delta = A(P, T)[1/E(t) - 1/E_\infty(P, T)]$. Aging behavior and memory effects caused by combination of pressure and temperature perturbations were investigated to predict the experimental results. Detailed experimental technique and procedures have been described in earlier papers.

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PATH DEPENDENCE OF STRUCTURAL RELAXATION OF ELASTOMERIC GLASSES

by

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PATH DEPENDENCE OF STRUCTURAL RELAXATION OF ELASTOMERIC GLASSES

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ABSTRACT

The theoretical calculation based on the general solution of a multi-ordering-parameter model is extended to study the combined pressure and temperature effects on the relaxation of a polyurethane elastomeric glass (Solithane 113). Distinctively different relaxation behavior was produced at a point (P,T) with the glasses arrived at the point by different paths, along an isobar and along an isotherm. A general solution for the kinetics of a certain path takes the form,

$$\delta(t) = \delta_0 \phi(t, t_0) - \int_{t_0}^t (\Delta\alpha Q - \Delta\beta P) \phi(t, t') dt'$$

where the relaxation time involved in ϕ is an explicit function of P, T, P_f (fictive pressure), and T_f (fictive temperature). T and T_f , and P and P_f are mutually convertible by a relationship, $\delta\delta = \Delta\beta d(P - P_f) = \Delta\alpha d(T_f - T)$ in which both $\Delta\beta$ and $\Delta\alpha$ are functions of P and T. During the aging of the elastomeric glass, Young's modulus (\bar{E}) was measured at various intervals of aging time to monitor the variation of δ , the volumetric measure of departure from the equilibrium, related to \bar{E} by an equation, $\delta = A(P, T)[1/\bar{E}(t) - 1/\bar{E}_\infty(P, T)]$. Aging behavior and

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memory effects caused by combination of pressure and temperature perturbations were investigated to predict the experimental results. Detailed experimental technique and procedures have been described in earlier papers.

I. INTRODUCTION

Polymeric glasses may be formed by lowering temperature, increasing pressure or combining both as a result of gradual reduction of the rate of molecular motion. When the rate of cooperative rearrangement of polymer chain segments becomes the same order of magnitude as the rate of cooling or pressurizing, in other words, the relaxation time is comparable to the time scale of observation t , the glass transition of an amorphous polymer occurs. Glasses usually exist in a nonequilibrium state and will continuously relax toward the equilibrium state with a rate depending on the relaxation time. This phenomenon is commonly referred to as physical aging.

Theoretical considerations based on statistical mechanics [1-6] indicate that the glass transition is a thermodynamic transformation, assuming the freezing-in model of internal parameters [7]. However, owing to the knowledge that aging of a glass is a purely kinetic process [8,9] which is inherently related to the relaxation time, there seems to be a tendency at present to treat glass transition as a kinetically controlled process [10,11]. The kinetic aspects of glass transition subject to different kinds of thermal treatments, such as quenching, annealing and temperature jump, etc. have been studied extensively [8-14] at atmospheric pressure. In addition to phenomenological description of kinetic aging, other theoretical considerations, based on statistical mechanics using hole diffusion process model [15] and stochastic model [16,17] have been proposed to explain the mechanism of kinetics at molecular level. In this study, investigations have been made to determine the combined effects of thermal and pressure treatments on the glass transition and

the relaxation. The basic kinetic equations and the expression for the relaxation time are modified to be both temperature and pressure dependent. Theoretical predictions from the general solution of these equations are then compared with the experimental results for a polyurethane elastomer (Solithane 113, $T_g = -20^\circ\text{C}$). The Young's modulus has been chosen as the parameter in monitoring the aging process. It was found that the structural recovery of elastomeric glass is strongly path dependent on the P-T-V space. Multi-ordering parameter model can be used to distinguish one glass from another at the same pressure and temperature but with different pressure-temperature history.

II. FUNDAMENTAL

THERMODYNAMIC CONSIDERATION

As shown previously [5], in the PVT space, the rubbery or the liquid state of an amorphous polymer, usually regarded as in equilibrium, can be represented by a liquid (L) surface of which the differential equation takes the form

$$dV_L = V_L \alpha_L(P, T) dT - V_L \beta_L(P, T) dP \quad (1)$$

whereas, the glasses in a nonequilibrium state must be identified with another parameter ξ_1 besides T and P. So that, the variation of volume of a glass is described by

$$dV_G = V_G \alpha_G(P, T) dT - V_G \beta_G(P, T) dP + \left. \frac{\partial V_G}{\partial \xi_1} \right|_{P, T} d\xi_1 \quad (2)$$

For constant values of ξ_1 , $d\xi_1 = 0$, there should be a family of iso- ξ_1 surfaces, each representing a specified glass. A glass specified by P, T, ξ_1 , will continuously reduce its volume by increasing ξ_1 toward equilibrium surface during aging at given P and T, signifying a consecutive variation from one specified glass to another.

The volume change $\left. \frac{\partial V_G}{\partial \xi_1} \right|_{P,T} d\xi_1$, responsible for the relaxation, can be shown to be equal to $V\Delta\alpha dT_f$ [5] by introducing the concept of fictive temperature T_f , referring to the PVT space (Fig. 1). A similar concept, namely, fictive pressure P_f , can be introduced and we can then establish the following relation,

$$\left. \frac{\partial V_G}{\partial \xi_1} \right|_{P,T} d\xi_1 = V\Delta\alpha dT_f = -V\Delta\beta dP_f \quad (3)$$

Figure 1 illustrates the relationship among V , P , T , P_f and T_f . The point O , which is on the ξ_0 -plane [5], specifies the current volume. By drawing an isobaric plane through O (see Fig. 1) and locating the intersection point of three planes; ξ_0 -plane, isobaric plane, and liquid plane, the fictive temperature T_f is obtained. A similar procedure with ξ_0 -plane, isothermic plane, and the liquid plane, determines the fictive pressure P_f . The fictive temperature T_f and fictive pressure P_f coincide at point Q which represents the equilibrium. Usually the liquid surface may not be a plane, since $\Delta\alpha$ and $\Delta\beta$, or α_L and β_L , are not constants as shown by Table 1.

KINETIC CONSIDERATION

A. Basic Equation

The kinetics of physical aging phenomenon is conventionally delineated by the relative departure from the equilibrium, using a dimensionless parameter, $\delta = (V - V_\infty)/V_\infty$, for isobaric process [8,11]. Furthermore, it can be extended to include variation of both T and P .

The multi-ordering parameter model, proposed by Kovacs et al. [8] and then developed by many others [9-14], partitions the δ into a number of sub-elements such that

$$\delta = \sum_{i=1}^N \delta_i. \quad (4)$$

The variation of each individual δ_i with time, under the concomitant heating rate q and pressurizing rate p , should be governed by the distinct differential equations

$$\frac{d\delta_i}{dt} = -\frac{\delta_i}{\tau_i} - \Delta\alpha_i q + \Delta\beta_i p \quad i = (i=1, 2 \dots N) \quad (5)$$

where $\Delta\alpha_i(P, T)$ and $\Delta\beta_i(P, T)$ are the difference in thermal expansivity and compressibility, respectively, between the liquid and the glassy states of the i -th element and τ_i is the corresponding relaxation time.

Summing up the solutions of the distinct equations (5), in the limit of large value N , with initial conditions given, we obtain the basic equation governing the volume relaxation as

$$\delta(t) = \delta_0 \phi(t, t_0) - \int_{t_0}^t [\Delta\alpha(P, T)q(t') - \Delta\beta(P, T)p(t')] \phi(t, t') dt' \quad (6)$$

where $\Delta\alpha$ and $\Delta\beta$ are functions of P and T , whereas $q(t) = dT/dt$ and $p(t) = dP/dt$ are the prescribed thermal and pressure treatment history. The Williams-Watt [18] function is employed for evaluating the response function ϕ in Eq. (6)

$$\phi(t, t') = \exp \left[- \left(\int_{t'}^t \frac{dt''}{\tau[T(t''), P(t''), T_f(t'')]} \right)^B \right] \quad (7)$$

in which, near the transition where $\Delta\beta$ and $\Delta\alpha$ do not vary substantially, T , T_f , P and P_f can be mutually converted by the relation

$$\delta = \Delta\alpha(T_f - T) = \Delta\beta(P - P_f) \quad (8)$$

At points (P, T) far away from the transition, the differential of Eq. (8) gives

$$\begin{aligned}
 d\delta &= \Delta\alpha(T_f, P) dT_f - \Delta\alpha(T, P) dT \\
 &= \Delta B(T, P) dP - \Delta B(T, P_f) dP_f
 \end{aligned}
 \tag{9}$$

The integral forms of Eq. (9) for an isotherm and isobar are, respectively, shown to be

$$\begin{aligned}
 \Delta\delta|_T &= \int_{P_0}^P \Delta B(T, x) dx - \int_{P_{f0}}^{P_f} \Delta B(T, y) dy \\
 \Delta\delta|_P &= \int_{T_{f0}}^{T_f} \Delta\alpha(x, P) dx - \int_{T_0}^T \Delta\alpha(y, P) dy
 \end{aligned}
 \tag{10}$$

B. Relaxation Time

In this work, the relaxation time τ depends on T , P and δ . When the pressure is atmospheric pressure, we set $P = 0$ and Arrhenius equation is expressed as [19,20]

$$\tau = A \exp \left[\frac{x E}{RT} + \frac{(1-x) E}{RT_f} \right]
 \tag{11}$$

When glasses are formed at different but constant pressures with the same cooling rate, crossing their respective T_g , the relaxation time for each glass should take the same value, i.e., $\tau|_P = \text{const.}$ [21]. Moreover, at the transition temperature, $T = T_f = T_g$, the following relation should hold:

$$\frac{E_p}{RT_g(P)} = \frac{E}{RT_g} \Big|_{\text{atm.}}
 \tag{12}$$

Therefore, E_p may be expressed as,

$$E_p = E \frac{T_g(P)}{T_g} = F \left(1 + \frac{b}{a} P + \frac{c}{a} P^2 + \dots \right)
 \tag{13}$$

in which E_p and E are the activation energies near equilibrium under pressure P and atmosphere, respectively. The pressure dependence of the glass transition temperature, $T_g(P)$, can be expressed for a general glass [5] transition line in Fig. 2 as

$$T_g(P) = a + bP + cP^2 + \dots \quad (14)$$

For solithane 113

$$a = T_g = 253, \quad b = 19, \quad c = -1.265$$

Tool's expression [19] for the relaxation time $\tau(T, \delta)$ at atmosphere is

$$\tau(T, \delta) = \tau_r a_\delta a_T \quad (15)$$

where τ_r is the reference relaxation time at T_r at equilibrium, and a_T and a_δ are the shift factors which may be obtained by use of Eq. (11), as

$$a_T = \frac{\tau(T, 0)}{\tau(T_r, 0)} = \exp\left[\frac{E}{R} (T^{-1} - T_r^{-1})\right] = \exp\left[\frac{E}{RTT_r} (T_r - T)\right]$$

$$a_\delta = \frac{\tau(T, \delta)}{\tau(T, 0)} = \exp\left[(1-x) \frac{E}{RTT_f} (T - T_f)\right] = \exp\left[-(1-x) \frac{E}{RTT_f} \frac{\delta}{\Delta\alpha}\right]$$

Instead of attempting to set forth a new shift factor a_p in addition to a_δ and a_T , we express the $\tau(T, P, \delta)$ in terms of P in the following manner,

$$\tau(T, P, \delta) = \tau_r a_\delta(P) a_T(P) \quad (16)$$

where

$$a_T(P) = \exp\left\{\frac{E(P)}{RTT_r(P)} [T_r(P) - T]\right\}$$

$$a_\delta(P) = \exp\left\{(1-x) \frac{E(P)}{RTT_f} (T - T_f)\right\}$$

Equation (13) still holds for E_p in the above expressions. As long as the reference relaxation time τ_r is assigned a unique value at each pressure, the corresponding $T_r(P)$ has to conform to the following relation as a result of Eq. (11) at equilibrium

$$\left. \frac{E}{RT_r} \right|_{\text{atm}} = \frac{E(P)}{RT_r(P)} \quad (17)$$

This leads to the same relation as $T_g(P)$, i.e.,

$$T_r(P) = T_r \left(1 + \frac{b}{a} p + \frac{c}{a} p^2 \right) \quad (18)$$

We have determined that the theoretical calculations could not predict the memory effect (Part V) for which the structural recovery gave rise to a broad δ peak as a function of aging time. The calculated half-width of the peak is too narrow to coincide with the experimental data. To broaden the peak of theoretical curves, we varied the model constants in Eq. (11), of which x proved most effective. However, a broader peak beyond the range $0 < x < 1$ was still required. Therefore, we have further modified Eq. (11) by separating apparent activation energies into two parts, one for the temperature and the other for the structure dependence as

$$\tau = A \exp \left[\frac{x E}{RT} + \frac{(1-x) E_s}{RT_f} \right] \quad (19)$$

where E_s is a function of $\delta = \Delta\alpha(T_f - T)$, indicative of structure dependence. Since Eq. (19) should reduce to the simple Arrhenius expression on the liquid line, where $T_f = T$, E_s must be a positive function approaching E when $T = T_f$, i.e.,

$$\begin{aligned} E_s &= E_s(T_f, T) > 0 \\ E_s(T_f, T_f) &= E_s(T, T) = E \end{aligned} \quad (20)$$

Thus, a simple relationship can be adopted between E and E_s as

$$E_s = E[1 - \frac{B}{T} (T_f - T)] = E[1 - \frac{B}{T} \frac{\delta}{\Delta\alpha}] \quad (21)$$

implying that the activation energy contributed by the structure increases when the glass relaxes toward equilibrium, i.e. δ decreasing and approaching zero as limit. B is a material constant expressed as a proportionality function of x . Henceforth,

$$a_\delta(P) = \frac{\tau(T, P, \delta)}{\tau(T, P, 0)} = \exp\left[-(1-x) \frac{E(P)}{R} \left(\frac{1+B}{TT_f}\right)(T_f - T)\right] \quad (22)$$

If we choose $B = 2x/(1-x)$, then Eq. (22) takes the following form

$$a_\delta(P) = \exp\left[-(1+x) \frac{E(P)}{RTT_f} (T_f - T)\right] \quad (23)$$

which can predict the wide range of memory effect observed in our experiment.

III. CALCULATIONS PERTAINING TO ISOTHERMAL AND ISOBARIC RESPONSES NEAR THE TRANSITION

Setting $p = 0$ or $q = 0$ in Eq. (6) and then utilizing the response function (7) in which the expression for the relaxation time (16) and the conversion relation (9) are employed, isobaric and isothermal processes (T_f vs. T and P_f vs. P) can be described by the following equations:

for isobar at P ,

$$T_f = T + (T_{f0} - T_0)\phi(T, T_0) - \int_{T_0}^T \phi(T, T') dT' \quad (24)$$

$$\phi(T, T') = \exp\left[-\left(\frac{1}{q} \int_{T'}^T \frac{dT''}{\tau[T(t''), P, T_f(t'')]} \right)^B\right]$$

for isotherm at T ,

$$P_f = P + (P_{f0} - P_0)\phi(P, P_0) - \int_{P_0}^P \phi(P, P') dP' \quad (25)$$

$$\phi(P, P') = \exp \left[- \left(\frac{1}{P} \int_{P_0}^P \frac{dP''}{\tau[T, P(t''), T_f(t'')]} \right)^B \right]$$

where

$$T_f(f) = T + [P(t'') - P_f(t'')]\left[\frac{\Delta\beta}{\Delta\alpha}\right]_{P(t'')}$$

For Solithane 113, the numerical calculations performed throughout this paper are based on the model constants,

$$\theta = \frac{E}{RT_r^2} = 0.51, \quad [22] \quad x = 0.35, \quad \beta = 0.25$$

$$T_r = 263^\circ\text{K}, \quad \tau_r = 1 \text{ min}$$

and the functional forms of $\Delta\beta(P)$ and $\Delta\alpha(P)$ were obtained by interpolating the values given on Table 1 [22].

Figure 3 displays the temperature dependence of calculated fictive temperature at various pressures, $P = 0, 1, 2, 3$ Kb with cooling rate $q = -0.02^\circ\text{C/min}$. Each curve shows a transition region through which substantial departure of T_f from T can be observed. As the temperature decreases, but before T_g is reached, T_f of the polymer in liquid state is equal to T . The T_g under these pressures (Fig. 2, solid line) are respectively $253^\circ, 273^\circ, 283^\circ$ and 294°K , which are located somewhere at the beginning part of the transition region. Rectangular rule was used for numerical integration with $\Delta T = 0.1$. The inadequacy caused by such a step length should be tolerable [11]. Figure 4 shows the pressure dependence of calculated fictive pressure at various temperatures, namely $T = 273^\circ, 283^\circ$, and 294°K , corresponding respectively to $P_g = 1, 2, 3$ Kb in which an equivalent

pressurizing rate $p = .0019 \text{ Kb/min}$ was used. As the pressure increases, but before P_g is reached, P_f of the polymer in liquid state is equal to P . The equivalent pressurizing rate is defined as $p = -q \Delta\alpha/\Delta\beta$, obtained by equating $\Delta\alpha q$ to $-\Delta\beta p$ in Eq. (6), implying the comparable time scales of observation for an isobar with q and an isotherm with p . Figure 5 illustrates the variation of δ in terms of pressure along these isotherms. The direct comparison of T and P scans (Fig. 3 and 4), which is made possible by a pure kinetic consideration incorporating the three-dimensional space scheme (Fig. 1), demonstrates their correspondence to each other near the glass transition. The two scans differ in that the isobaric glass relaxes more slowly during cooling below T_f than the isothermic glass during pressurizing above P_f . That is, T_f from P scan in the glass region decreases less sharply than P_f in T scan increases. The T_f or P_f would remain constant if the relaxation completely ceases.

IV. PHYSICAL AGING OF GLASSES FORMED BY DIFFERENT P-T PATHS

Elastomeric glasses of Solithane 113 formed via either isobaric or isothermal paths were studied at various states of pressure and temperature for their aging behavior in this high pressure laboratory [23,24]. Young's moduli (\bar{E}) were measured at various intervals of aging to monitor the variation of δ through a relation,

$$\delta = A(P,T) \left[\frac{1}{\bar{E}(t)} - \frac{1}{\bar{E}_\infty(P,T)} \right] \quad (26)$$

where $\bar{E}(t)$ is the instantaneous Young's modulus measured at aging time t , $\bar{E}_\infty(P,T)$ is the equilibrium Young's modulus and A the proportionality function to be determined from the experimental data of the aging at (T,P) of a special glass formed along a prescribed path.

Theoretical calculations, based on the general solution of the multi-ordering-parameter, Eq. (6), and response function, Eq. (5), have to be coupled with the conversion relation

$$d\delta = \Delta B(p)dp - \Delta B(P_f)dP_f = \Delta\alpha(T_f)dT_f$$

for an isothermal path, or

(27)

$$d\delta = -\Delta B(p_f)dP_f = \Delta\alpha(T_f)dT_f - \Delta\alpha(T)dT$$

for an isobaric path. In Fig. 6 and 7, δ is plotted against time for each glass formed by first lowering temperature along an isobar ($p = 0$) respectively to different temperatures, viz. 15°, 4.5°, -6.5°, -25°C at $q = -0.5^\circ\text{C}/\text{min}$ and then applying pressure to 3 Kb at a rate $p = 0.25 \text{ Kb}/\text{min}$ along the isotherms. The data points which were converted from the $\bar{\epsilon}$ measurement [24], begin one hour after aging starts. The δ versus the aging time for glasses formed by first applying pressure to 3 Kb along the 35°C isotherm, then lowering temperature respectively for each glass to the desired level, viz. 15°, 4.5°, -6.5° and -25°C along the 3 Kb isobar at the same p and q . It is observed from these curves that the higher the temperature of aging, the lower the δ is (Figs. 6 and 7) because the glass is closer to the equilibrium temperature (18°C at 3 Kb) and that the higher the temperature, the faster the relaxation is as revealed by the steeper slope of the curves (Figs. 8 and 9) because the relaxation time is shorter at higher temperatures. Figure 10 shows the P_f vs. P for the isotherms. Each curve has a transition zone before 3.0 Kb is reached except at -25°C which is already below the glass transition temperature under 0 Kb.

V. MEMORY BEHAVIOR

The memory effect associated with two consecutive temperature perturbations at reasonably slow rate of cooling and heating has been studied extensively by many

investigators [8-14]. In the present work, calculations were made to predict the memory behavior of Solithane 113 subject to pressure and temperature perturbations.

The experimental procedure was as follows:

1. The original glass (the control sample) was formed by pressurizing Solithane to 2.5 Kb with $p = .25 \text{ Kb/min}$ at 15°C as shown in Fig. 2.
2. The control sample was immediately given a pressure perturbation, $\Delta P = 0.5 \text{ Kb}$, that is pressured to 3 Kb (Step 1).
3. The sample was then aged at 3 Kb for 10 hours (Step 2).
4. The pressure was reduced back to 2.5 Kb at $p = -0.5 \text{ Kb/min}$ (Step 3).
5. The sample was allowed to undergo relaxation at 2.5 Kb and 15°C , the Young's modulus measured at various aging times (Step 4) and the δ obtained.
6. The same procedure was followed with $\Delta P = 1.5 \text{ Kb}$ and $\Delta P = 2 \text{ Kb}$.

The resulting δ exhibits a peak due to memory effect by the pressure perturbation as shown in Fig. 11 and 12. Equation (16) modified to include these four steps with initial condition, $\delta_0 = 0$ ($P_0 = P_{f0}$) at t_0 , can be written as

$$\delta(t) = p_1 \int_{t_0}^t \Delta B(t') \phi(t, t') dt'$$

where $t_0 \leq t < t_1$ (Step 1)

$$= p_1 \int_{t_0}^{t_1} \Delta B(t') \phi(t, t') dt'$$

where $t_1 \leq t < t_2$ (Step 2)

$$= p_1 \int_{t_0}^{t_1} \Delta B(t') \phi(t, t') dt' + p_2 \int_{t_2}^t \Delta B(t') \phi(t, t') dt'$$

where $t_2 \leq t < t_3$ and p is zero between t_1 and t_2 (Step 3)

$$= p_1 \int_{t_0}^{t_1} \Delta B(t') \phi(t, t') dt' + p_2 \int_{t_2}^{t_3} \Delta B(t') \phi(t, t') dt'$$

where $t_3 \leq t$ (Step 4)

(28)

The results of these isotherms are shown by the curves 1, 2, 3 ($\Delta p = 2.0, 1.5, 0.5$ Kb) in Fig. 11, together with curve 4 which shows the relaxation behavior of the control sample, that is relaxation of the original glass at 2.5 Kb and 15°C without pressure perturbation. These curves are reproduced in Fig. 12 without steps 1 to 3 in order to compare with the experimental data. Figure 13 shows how P_f changes during pressure perturbation cycle. As pressure is increased from atmospheric to 4 Kb, P_f increases from 0 to B, crossing A where T_g occurs; P_f increases from B to C, while P is held constant for 10 hours and P_f undergoes a change from C to D by first increasing slightly and then decreasing during depressurization from 4 to 2.5 Kb. The aging at 2.5 Kb and 15°C is represented by P_f going from D to E to F but never reaching 2.5 Kb. The detail of changes of P_f during the aging process (D to E to F in Fig. 13) is plotted against aging time in Fig. 14.

In temperature perturbation experiments, the samples were initially pressurized to 2.5 Kb at 15°C. Without waiting at that state, they were cooled down immediately to 10°, 5° and 0°C respectively; held at those temperatures for ten hours, heated back to 15°C and allowed to age and was tested for elastic response at various aging times. The rates of heating and cooling during the

process was $0.5^{\circ}\text{C}/\text{min}$ (q_2) and $-1.0^{\circ}\text{C}/\text{min}$ (q_1) respectively. The basic equation for the above process may be written as

$$\delta(t) = p_1 \int_{t_0}^t \Delta\beta(t')\phi(t,t')dt'$$

$$\text{where } t_0 \leq t < t_1$$

$$= p_1 \int_{t_0}^{t_1} \Delta\beta(t')\phi(t,t')dt' - q_1 \int_{t_1}^t \Delta\alpha(t')\phi(t,t')dt'$$

$$\text{where } t_1 \leq t < t_2$$

$$= p_1 \int_{t_0}^{t_1} \Delta\beta(t')\phi(t,t')dt' - q_1 \int_{t_1}^{t_2} \Delta\alpha(t')\phi(t,t')dt'$$

$$\text{where } t_2 \leq t < t_3$$

$$= p_1 \int_{t_0}^{t_1} \Delta\beta(t')\phi(t,t')dt' - q_1 \int_{t_1}^{t_2} \Delta\alpha(t')\phi(t,t')dt' \\ - q_2 \int_{t_3}^t \Delta\alpha(t')\phi(t,t')dt'$$

$$\text{where } t_3 \leq t < t_4$$

$$= p_1 \int_{t_0}^{t_1} \Delta\beta(t')\phi(t,t')dt' - q_1 \int_{t_1}^{t_2} \Delta\alpha(t')\phi(t,t')dt' \\ - q_2 \int_{t_3}^{t_4} \Delta\alpha(t')\phi(t,t')dt'$$

$$\text{where } t_4 \leq t$$

(29)

The results of the above calculations for the memory effect, i.e., δ versus aging time $(t-t_4)$ are plotted in Fig. 15. The calculated curves agree reasonably

well with experimental data [24].

ACKNOWLEDGEMENT

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TABLE 1. Physical Constants of Solithane 113

| P (Kb.) | T _α (K) | Δα (K ⁻¹ × 10 ⁴) | ΔB (Kb. ⁻¹) | ΔB/Δα (K/Kb.) | dT _α /dP (K/Kb.) |
|------------|-----------------------|--|----------------------------|------------------|--------------------------------|
| 0 | 275 | 4.9 | 1.80 | 37 | 18 |
| 1 | 292 | 2.8 | 0.78 | 28 | 15 |
| 2 | 305 | 2.4 | 0.53 | 22 | 12 |
| 3 | 316 | 1.7 | 0.29 | 17 | 11 |
| 4 | 326 | 1.3 | -- | -- | 10.5 |

FIGURE CAPTIONS

- Fig. 1: Interrelation between P_f , T_f , T and P on schematic of PVT space.
- Fig. 2: Pressure vs. transition temperature for Solithane 113.
- Fig. 3: Temperature dependence of calculated fictive temperature at various pressures.
- Fig. 4: Pressure dependence of calculated fictive pressure at various temperatures.
- Fig. 5: Pressure vs. variation of δ along isotherms.
- Fig. 6: δ vs. time for the treatment of glasses along prescribed paths (isotherms).
- Fig. 7: δ vs. time for the treatment of glasses along prescribed paths (isotherms).
- Fig. 8: δ vs. time for the treatment of glasses along prescribed paths (isobars).
- Fig. 9: δ vs. time for the treatment of glasses along prescribed paths (isobars).
- Fig. 10: P_f vs. P for isotherms on Fig. 6 and 7.
- Fig. 11: Theoretical results of isotherms with memory effect due to pressure perturbations.
- Fig. 12: Memory effect, $\delta \times 1000$ vs. aging time (Step 4 of Fig. 11).
- Fig. 13: P_f vs. P for curve 2 of Fig. 11.
- Fig. 14: P_f vs. time for curve 2 of Fig. 22.
- Fig. 15: Memory effect, $\delta \times 1000$ vs. aging time.

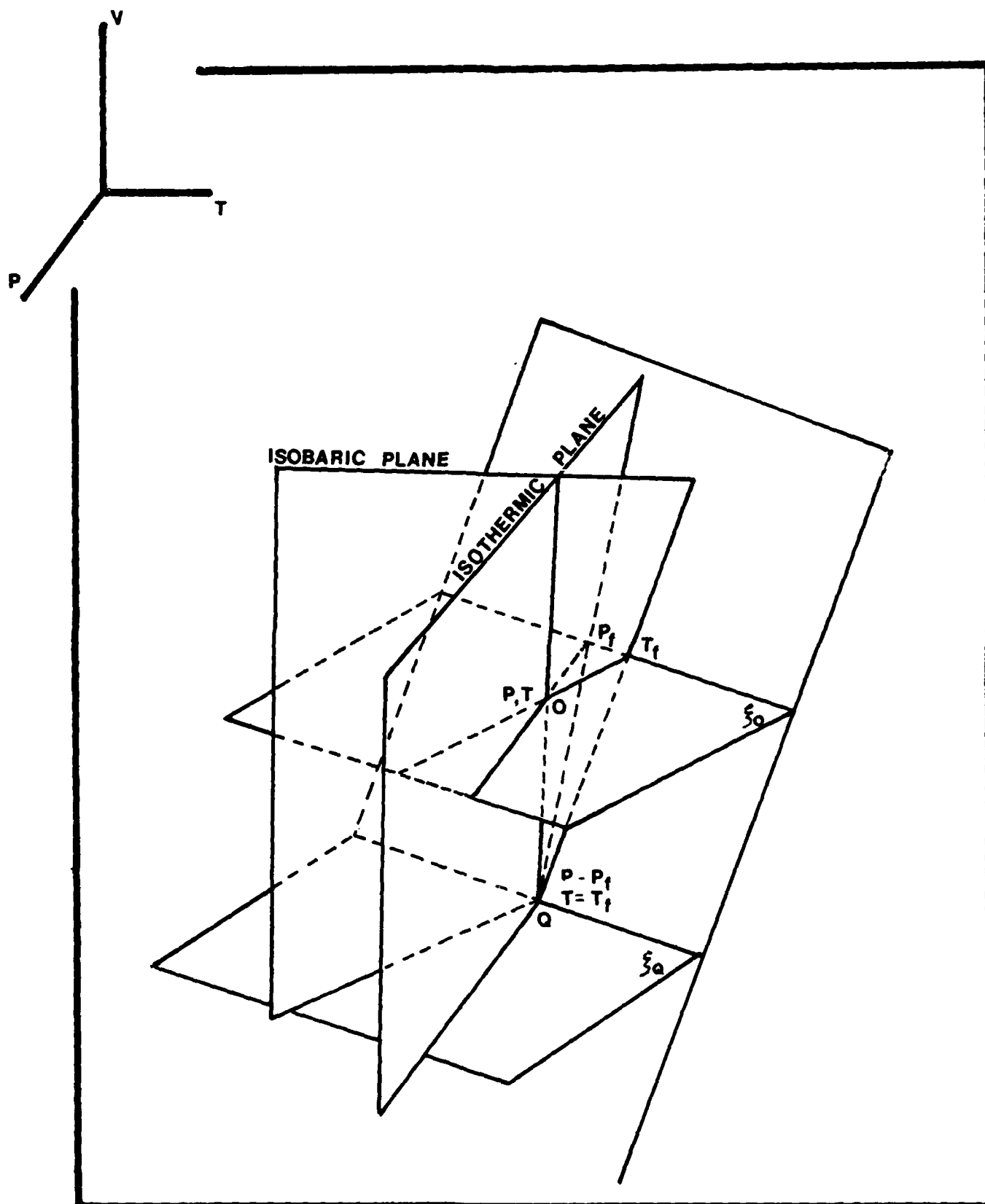


Fig. 1

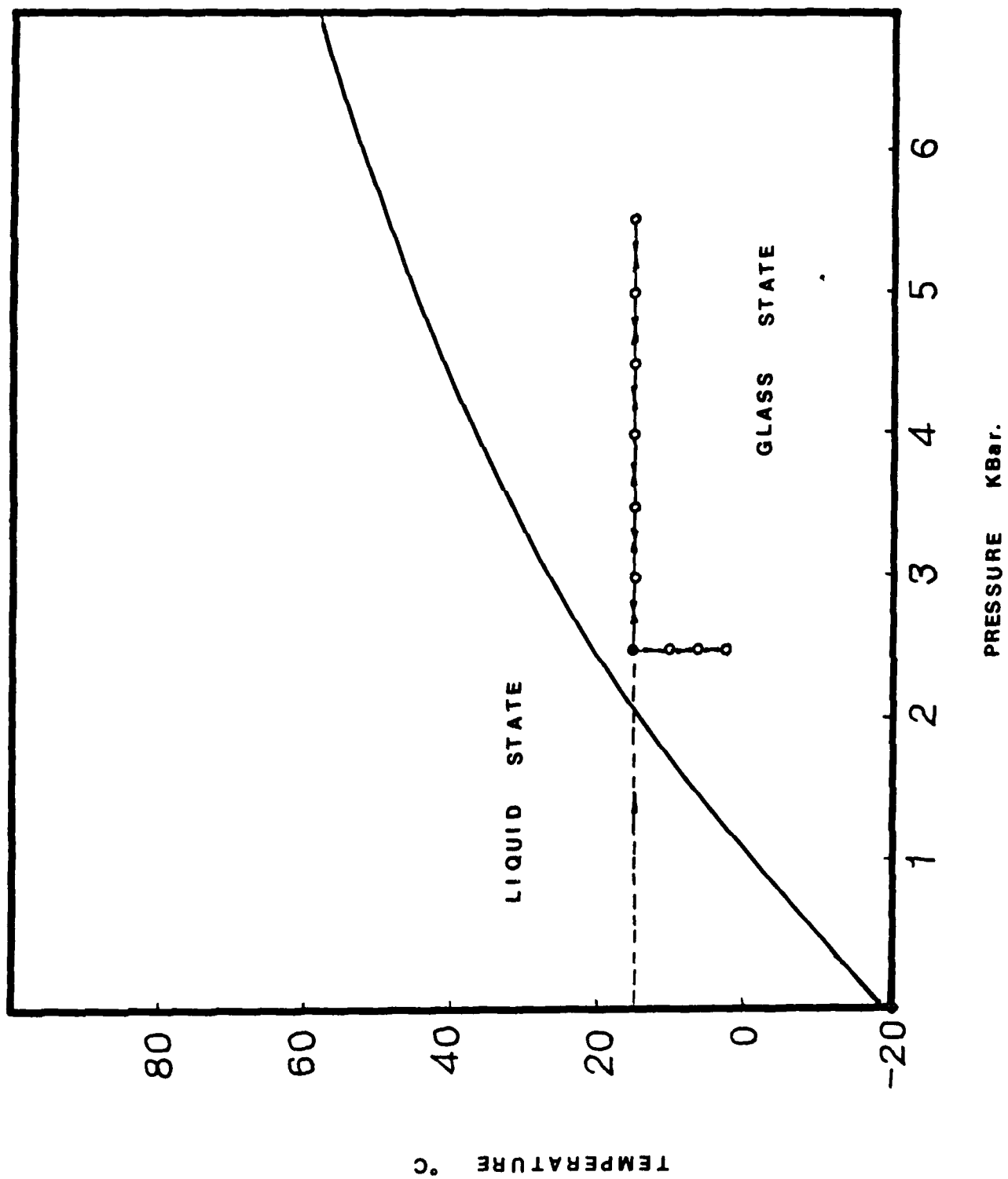


Fig. 2

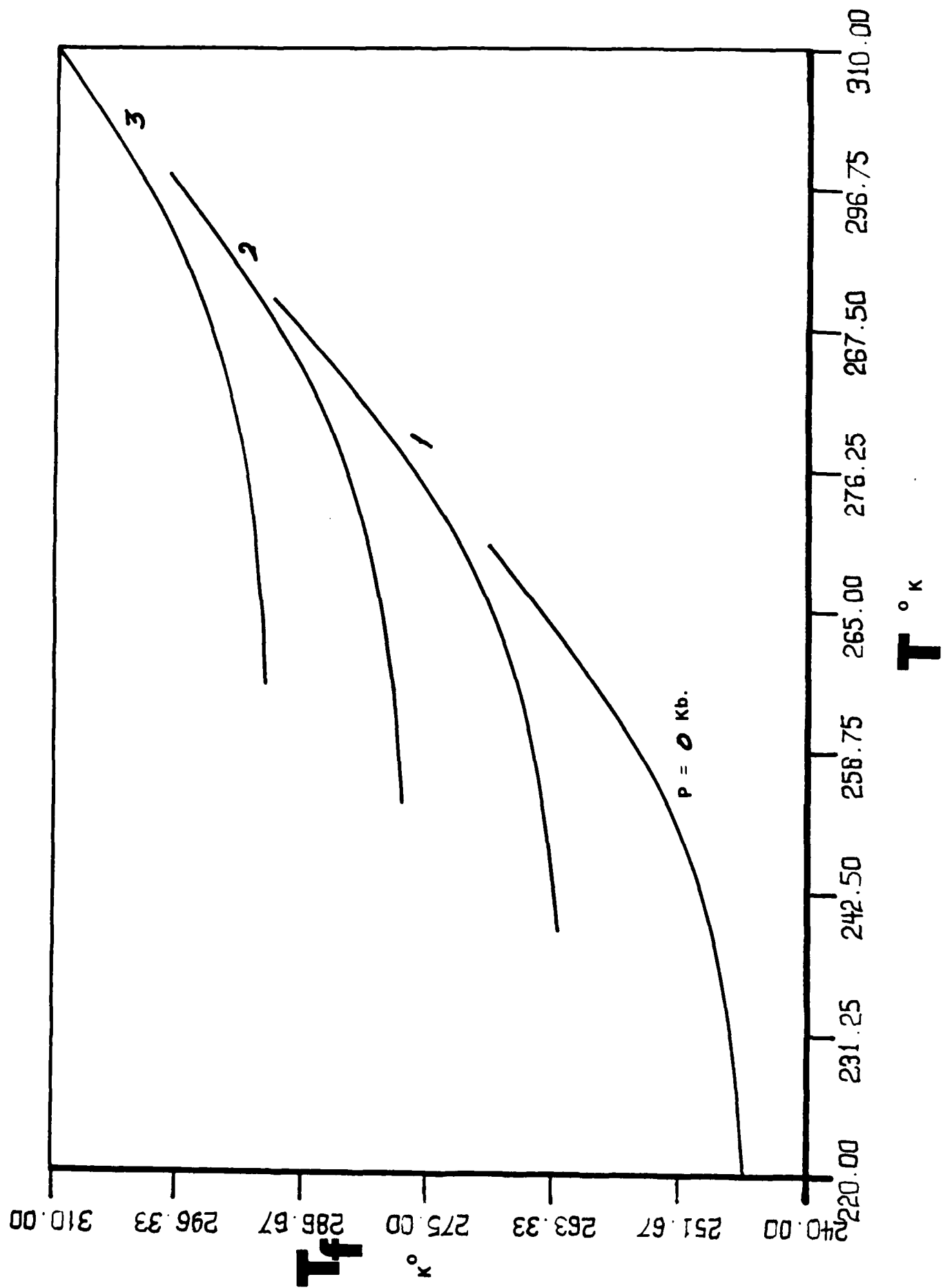


Fig. 3

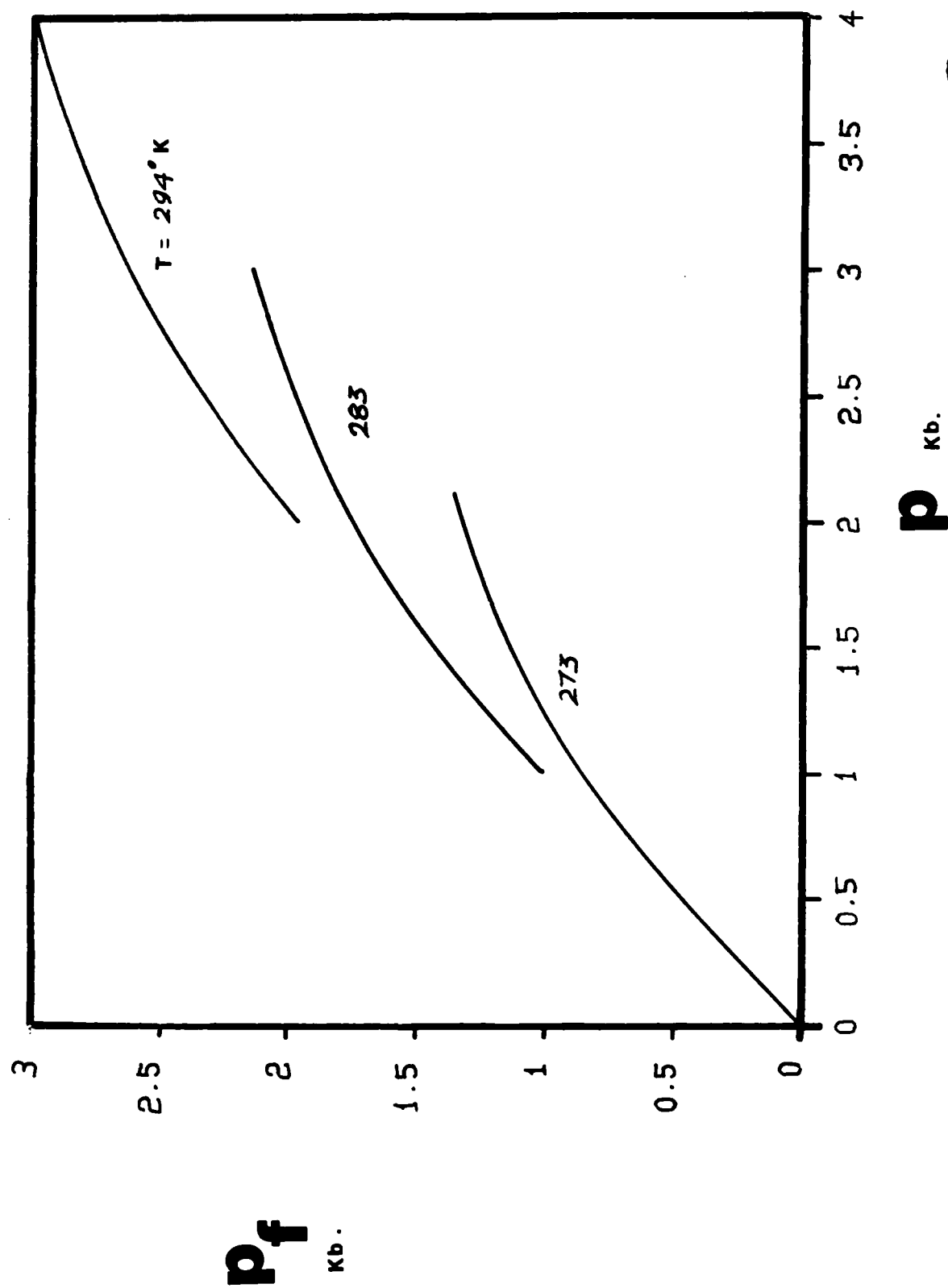
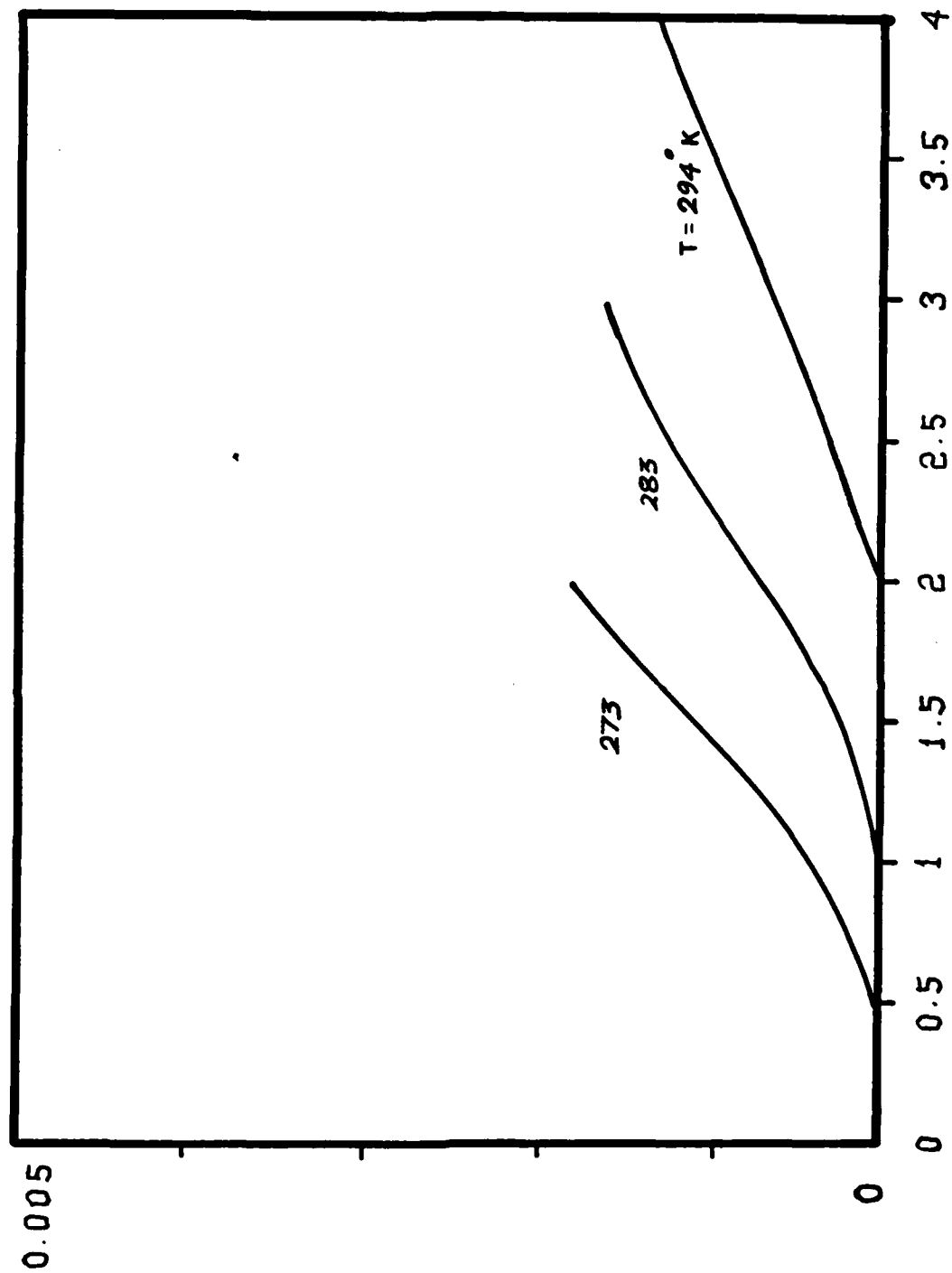


Fig. 4



p Kb.

Fig. 5

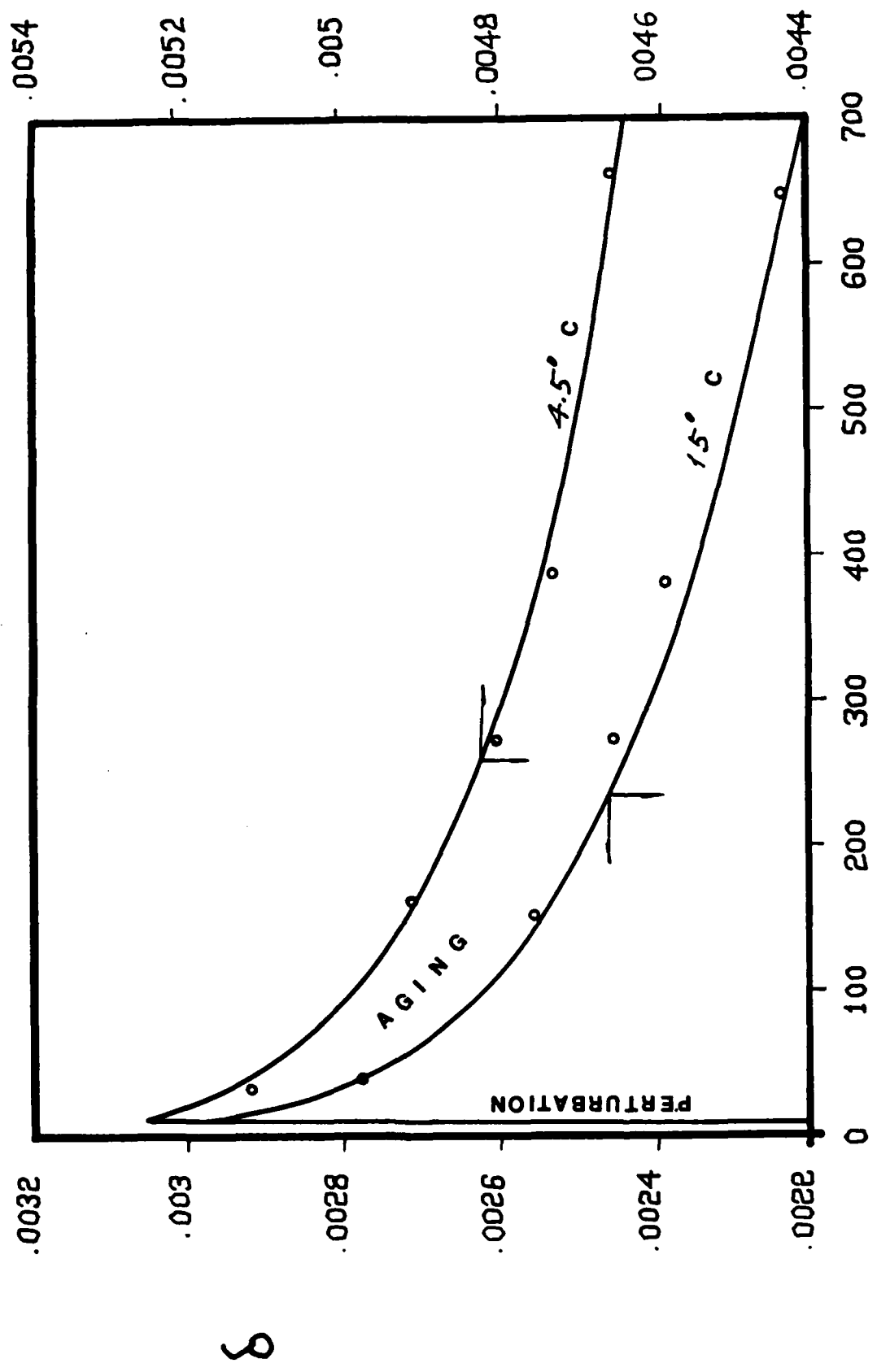


Fig. 6

TIME MIN.

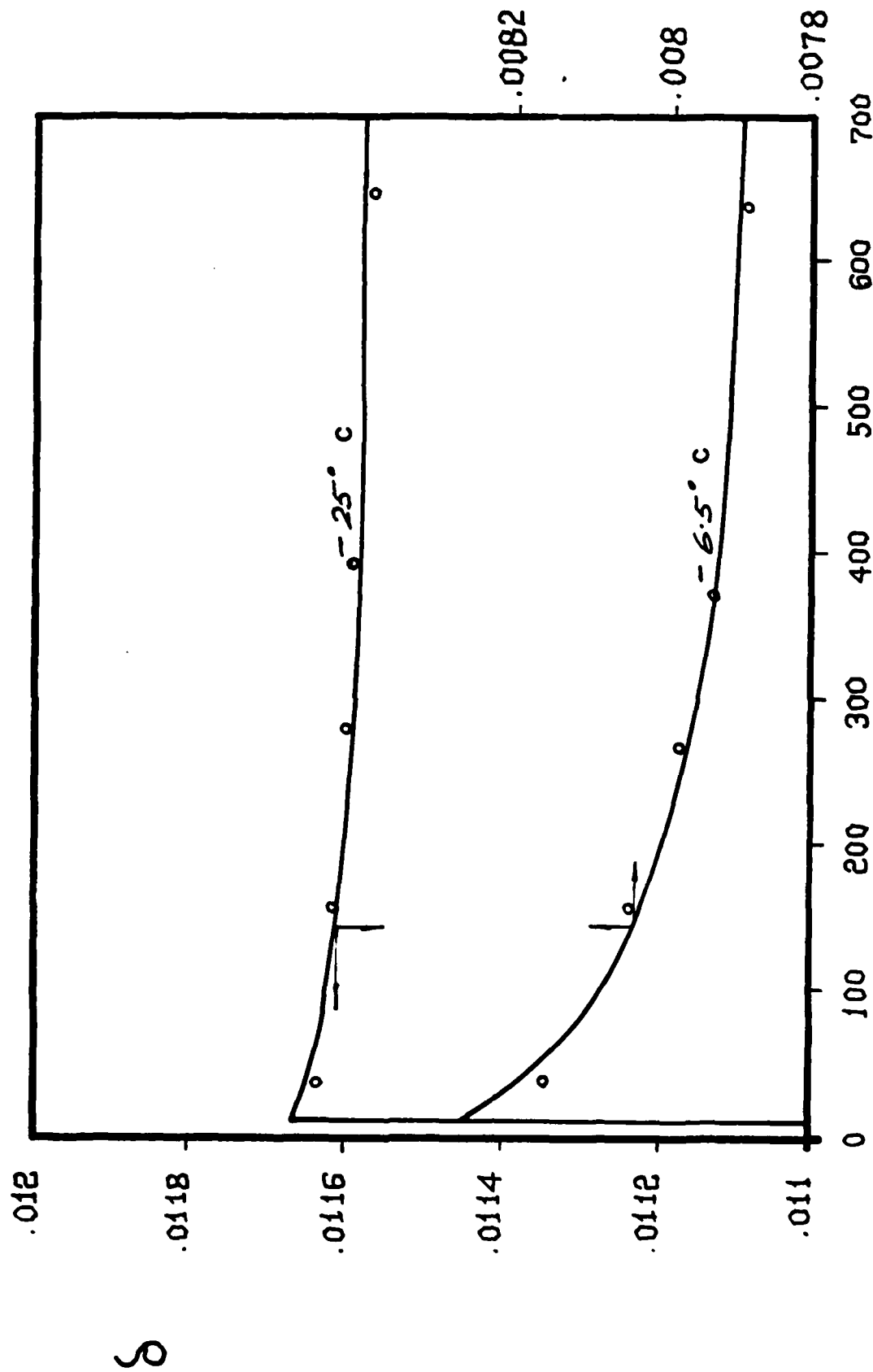


Fig 7

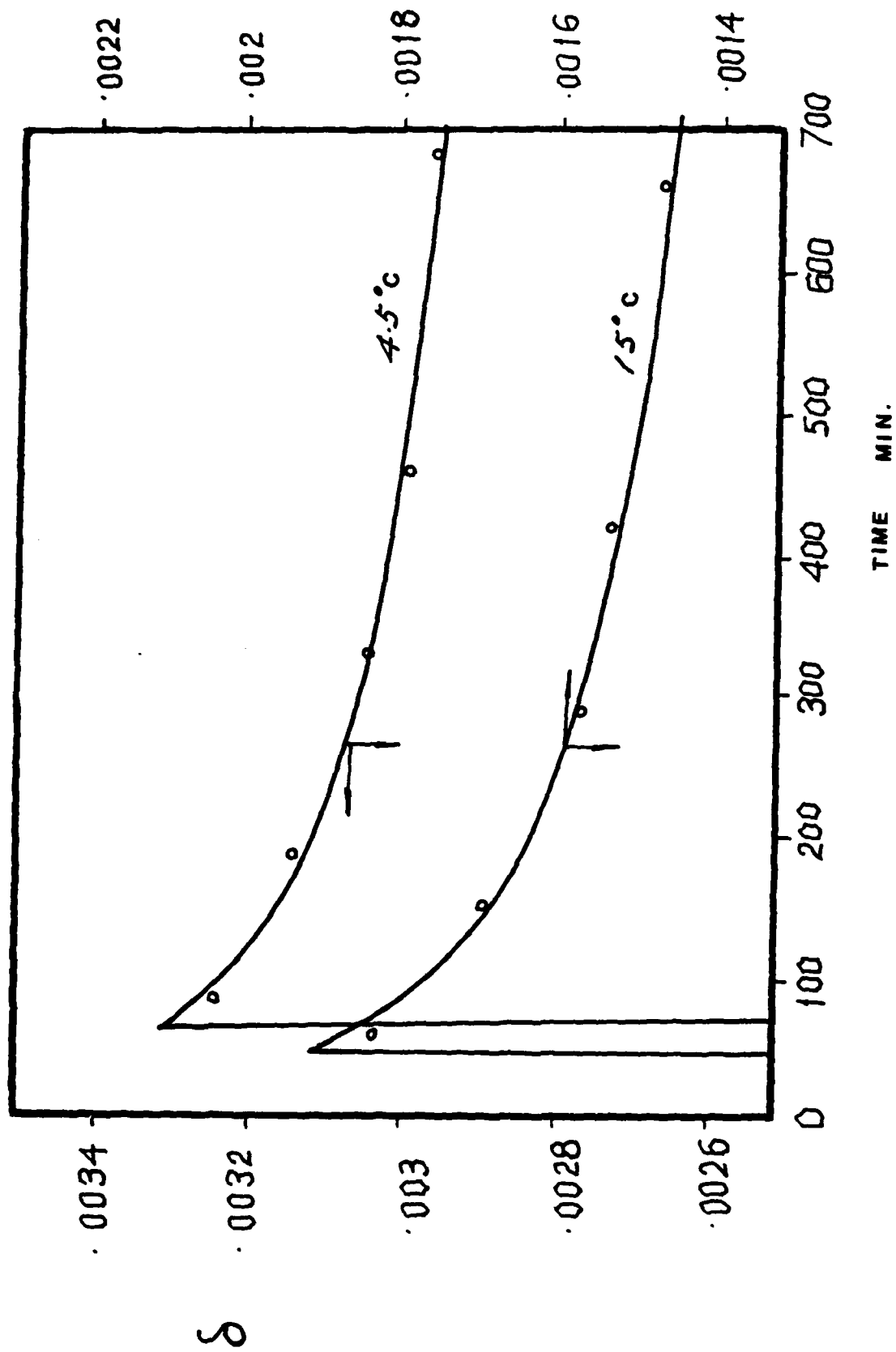


Fig. 8

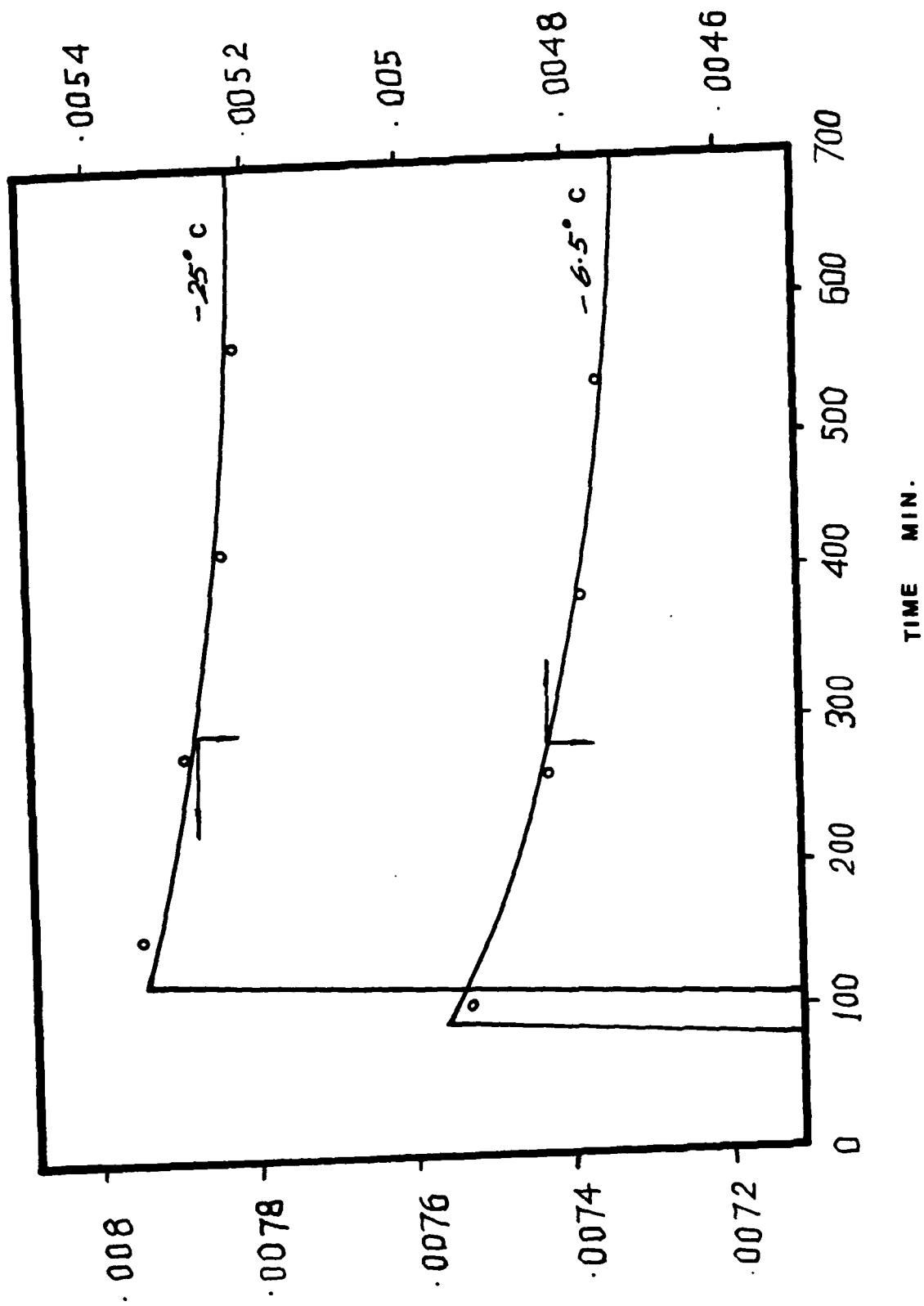


Fig. 9

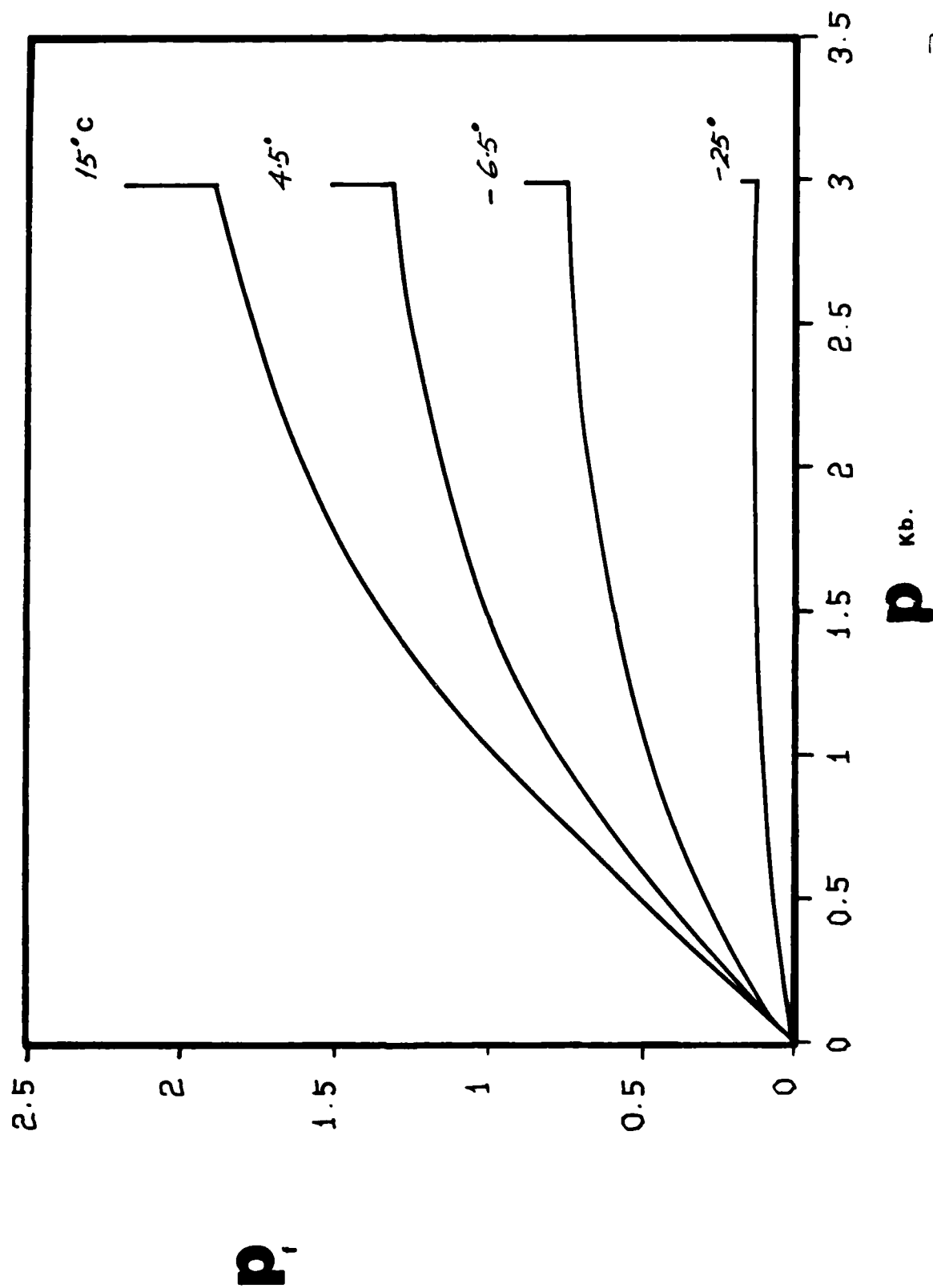


Fig. 10

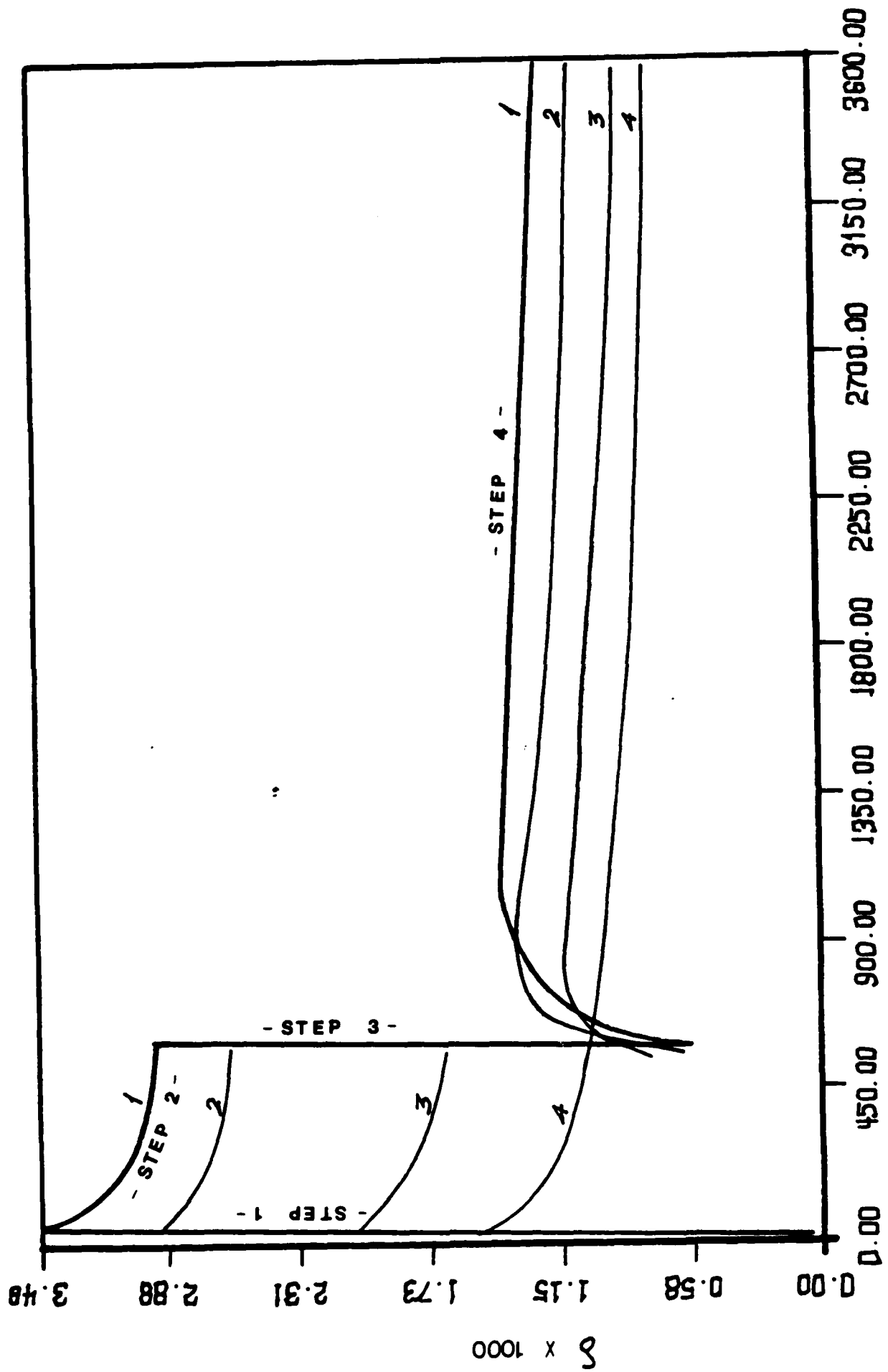
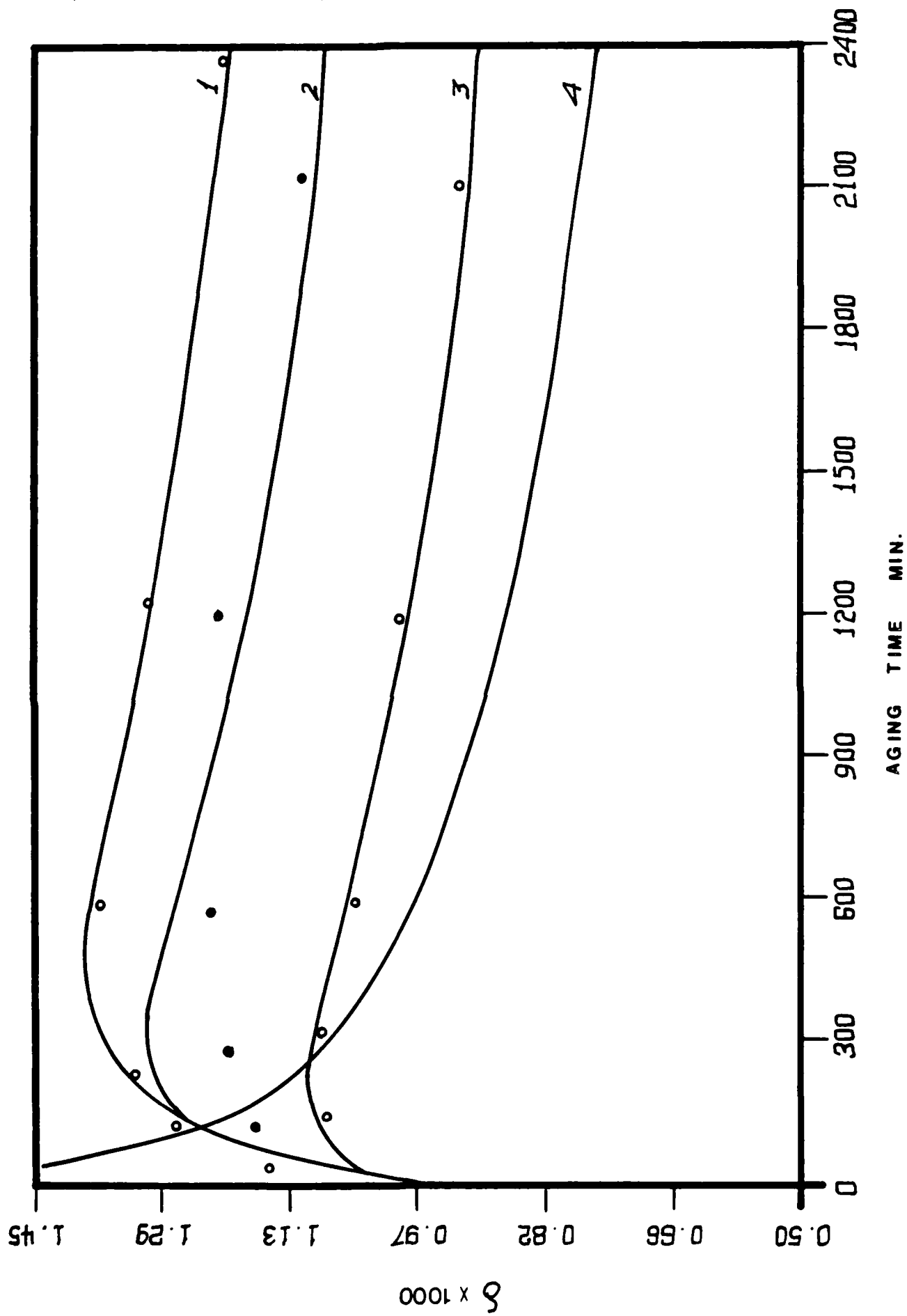


Fig. 11



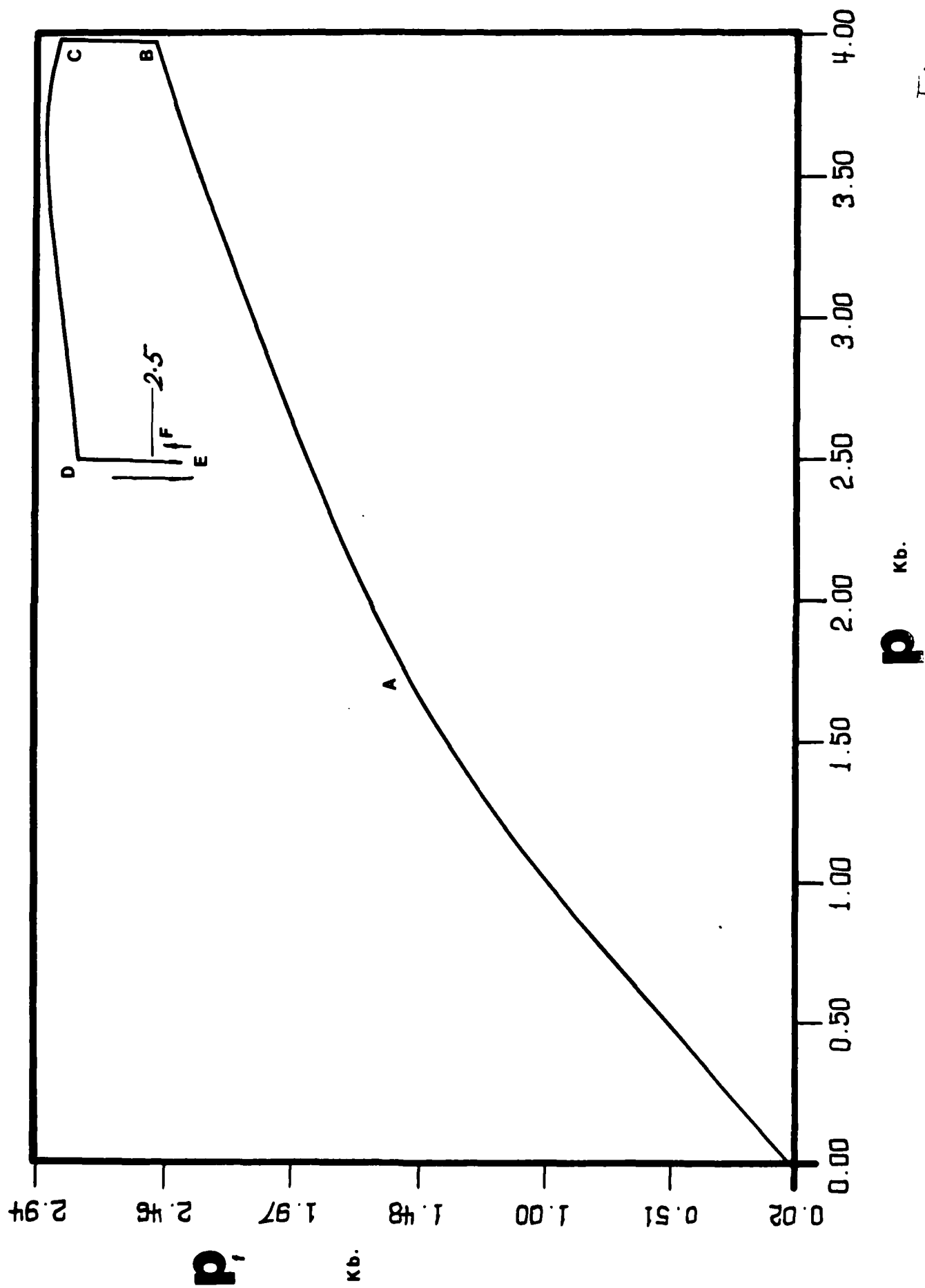
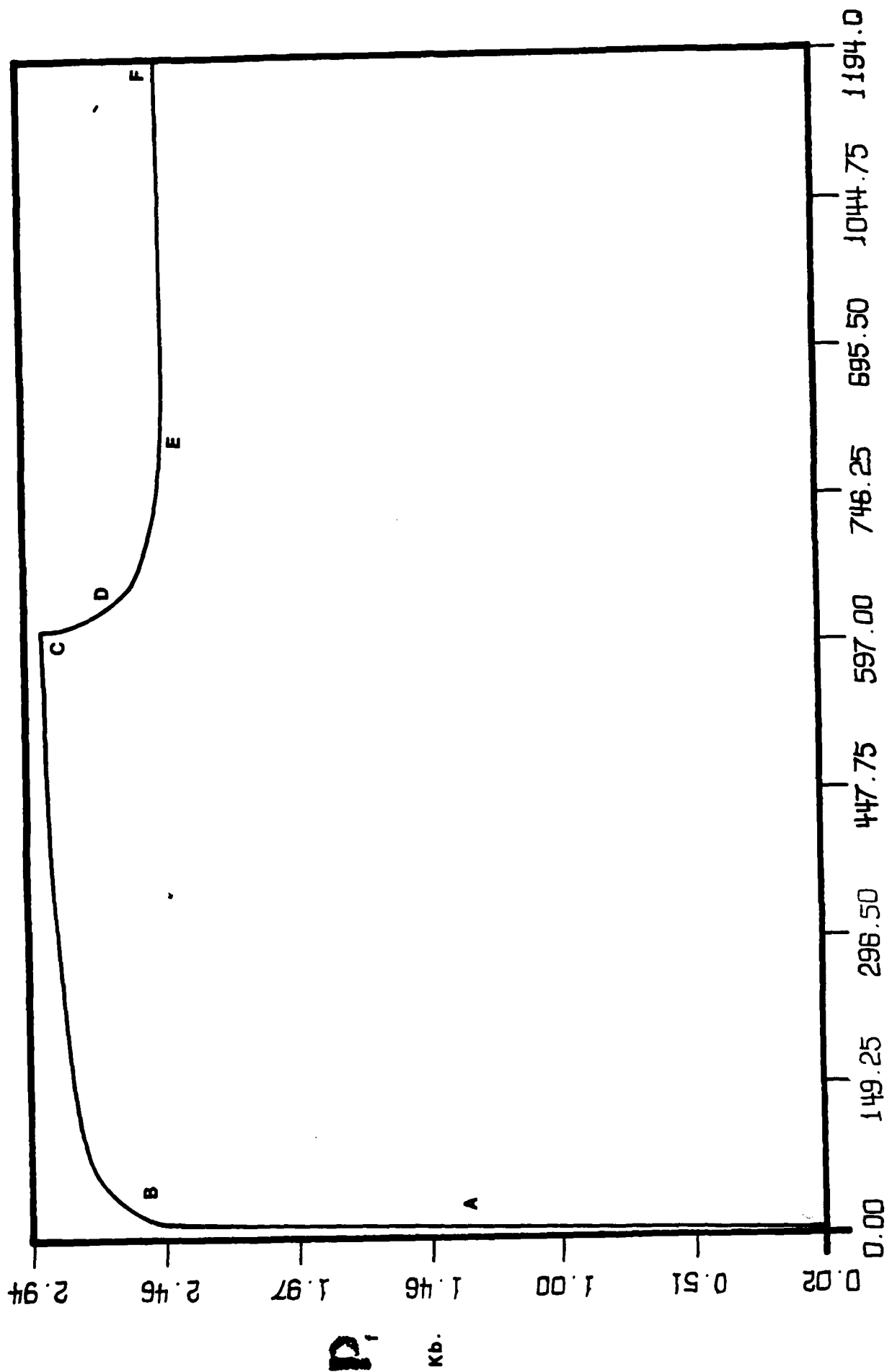


Fig. 13



TREATMENT TIME MIN.

Fig. 14

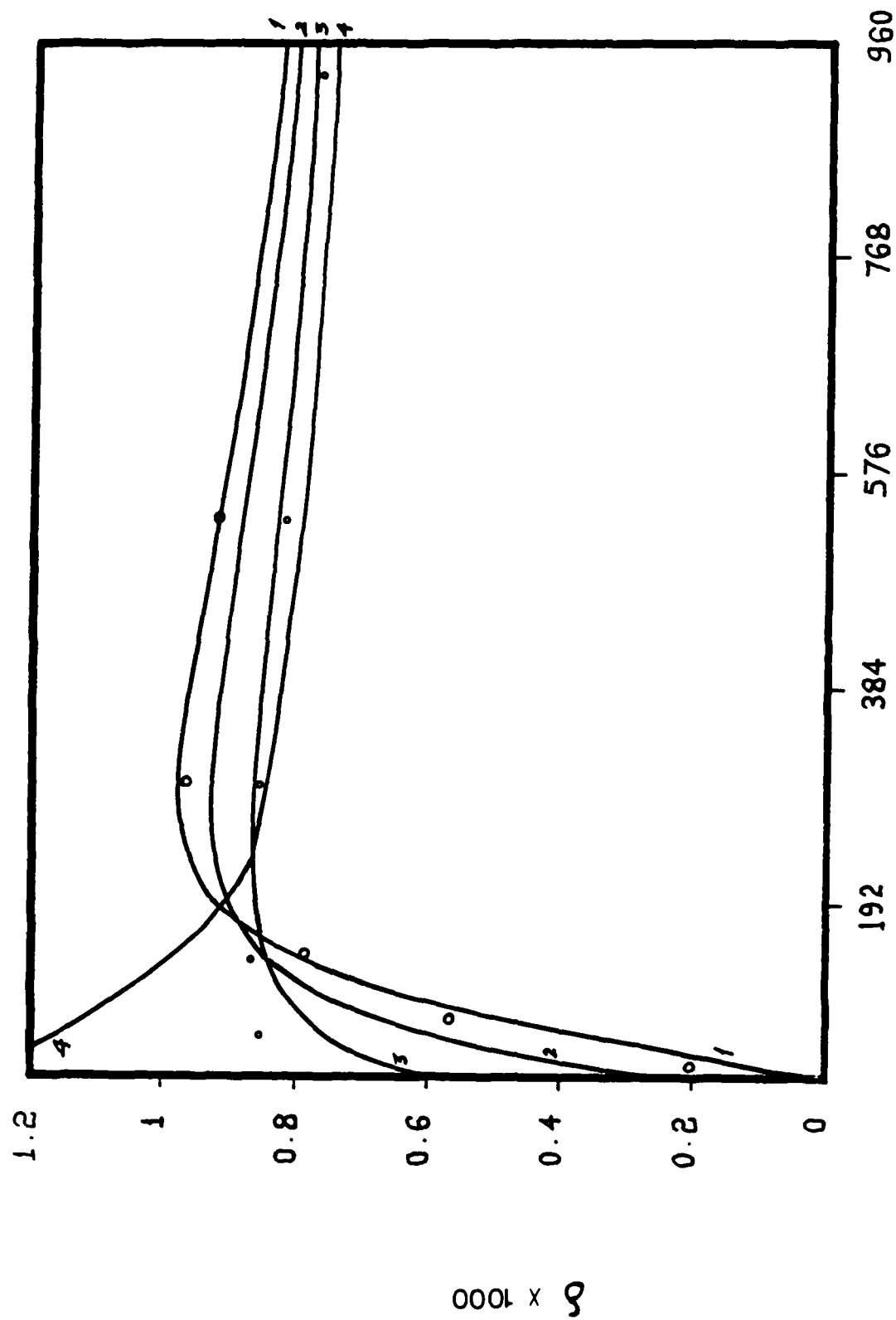


Fig. 15

AGING TIME MIN.

END

1-87

DTIC